GEORGIA INSTITUTE OF TECHNOLOGY

Engineering Experiment Station

PROJECT TERMINATION

Date June 30, 1970

PROJECT TITLE: Recovery of Attapulgite from Phosphorite Matrices

PROJECT NO: A-1208

PROJECT DIRECTOR: Mr. M. F. Munoz

SPONSOR: Kerr-McGee Corporation

TERMINATION EFFECTIVE: March 31, 1970

CHARGES SHOULD CLEAR ACCOUNTING BY: All acceptable charges have cleared.

Chemical Sciences & Materials Division

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EES 402 (R10—62)

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

B448 n2

PROJECT INITIATION

Date: October 13, 1969

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Project No.: A-1208

Project Director: Mr. M. F. Munoz

Sponsor: Kerr-McGee Corporation

Effective . . . . . October 1, 1969 . . . . . Estimated to run until: . . February 1, 1970 . . . . . .

Type Agreement: . Standard Industrial . . . . . Amount: $. 6,940.00 . . . . . .

Reports: Monthly Progress
Final Summary - due by March 1, 1970

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EA-62(12-66)

EXPERIMENTAL WORK

1. Preparation of the sample. The matrix sample for each bag received was chopped into 1/2 inch portions and placed back into the original containers. When the total sample was chopped, all the bags were emptied on a platform and the sample mixed by the cone-and-ring method. After mixing, the matrix was placed back into sealed containers to prevent evaporation.

2. Characterization of the sample. Mineralogical analyses of the fractions of matrix obtained in size distribution determinations are in progress.

X-ray diffraction analyses of the -325 mesh portion of the matrix show attapulgite as well as other clay minerals present. Electron micrographs (Figure 2) of the same fraction are enclosed. The needle-like habit of attapulgite particles is evident.

Moisture and dry density determinations were performed on the matrix. Results are shown in Table I.

3. Recovery and evaluation of recovered products. Preliminary work on separation of clay "chips" in the larger than 200 mesh size fraction indicate no clear-cut separation of the clay from the phosphorite and quartz. Electrophoretic techniques will be used prior to flotation testing, in order to use the flotation techniques at the most promising pH values for the recovery of the clay mineral.

Calcined Product. A sample of the minus 200 mesh portion of the matrix was treated as shown in Figure 1.: Flowsheet of Fuller's earth processing. The product obtained was tested and both the parameters of the test and the properties of the product are shown in Table II.

Discussion of Results

As it can be seen from Table II, the "calcined" material shows very good water absorption and satisfactory oil absorption. These values are approximately the values found in commercial products sold in supermarkets.

The product was obtained by an incomplete calcination of the clay. Complete calcination of attapulgite occurs above 1600°F when the elements constituting attapulgite recrystallize into eustatite, sillimanite and cristobalite.[1] The purpose of the heat treatment is to make the clay particle resistant to abrasion (dusting) and to avoid turning muddy on wetting. Several tests were made at different temperatures, and the material produced at 900°F seems to have the necessary consistency and oil and water absorption properties to yield a possible commercial product.

The amount of flocculant used was in excess of the amount needed to produce satisfactory flocs. More tests are planned to yield the optimum concentration of flocculant.

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[1] Calliere, S. and Henin, S., "The Sepiolite and Polygorskite Minerls" in The Differential Thermal Investigation of Clays, ed. by Robert C. McKenzie, London: The Mineralogical Society (Clay Minerals Group), 1959.

TABLE I

DRY DENSITY OF PHOSPHORITE MATRIX

Moisture: 27.1%

Sample No.	Dry Density, (lb/c. ft.)
1	79.3
2	77.5
Average of 2 samples	78.4

TABLE II

FULLER'S EARTH PROCESSING DATA

Drying temperature: 220°F

Size of Product "calcined": 8 x 20 mesh

"Calcination" temperature: 900°F

Kiln retention time: 20 minutes

Resistance to dusting: Fair

Oil and Water Absorption of "Calcined" Slimes

	Oil Absorption (%)	Water Absorption (%)
Average of two samples of calcined slimes	64.3	112.8
Commercial Product (Hartz Mountain)	70.0	100.0

Bulk Density of "Calcined" Slimes

	Bulk Density (lb/cu. ft.)
"Calcined" Slimes	30.3
Commercial Product	30.0

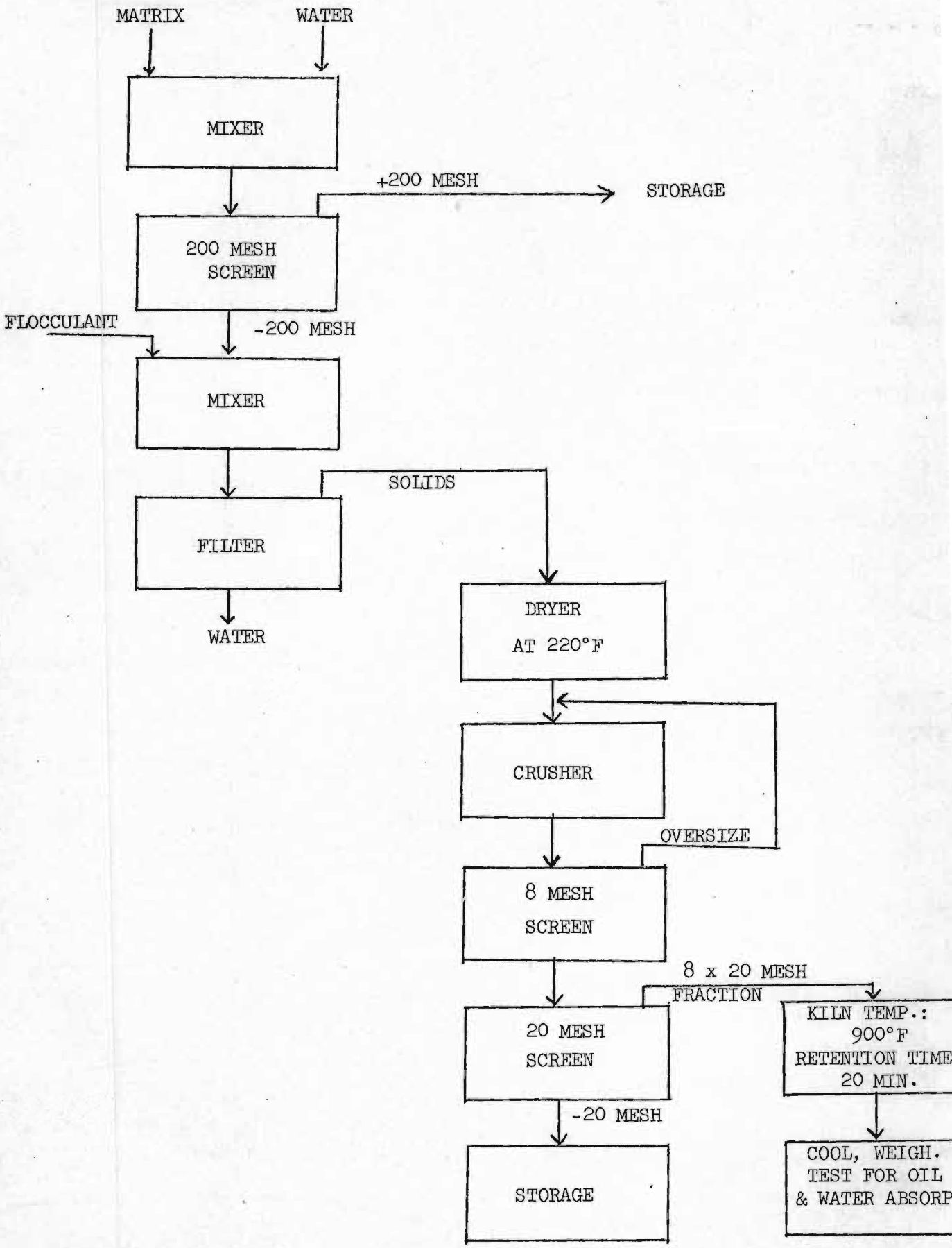

Fig. 1 Flowsheet of Fuller's Earth Processing

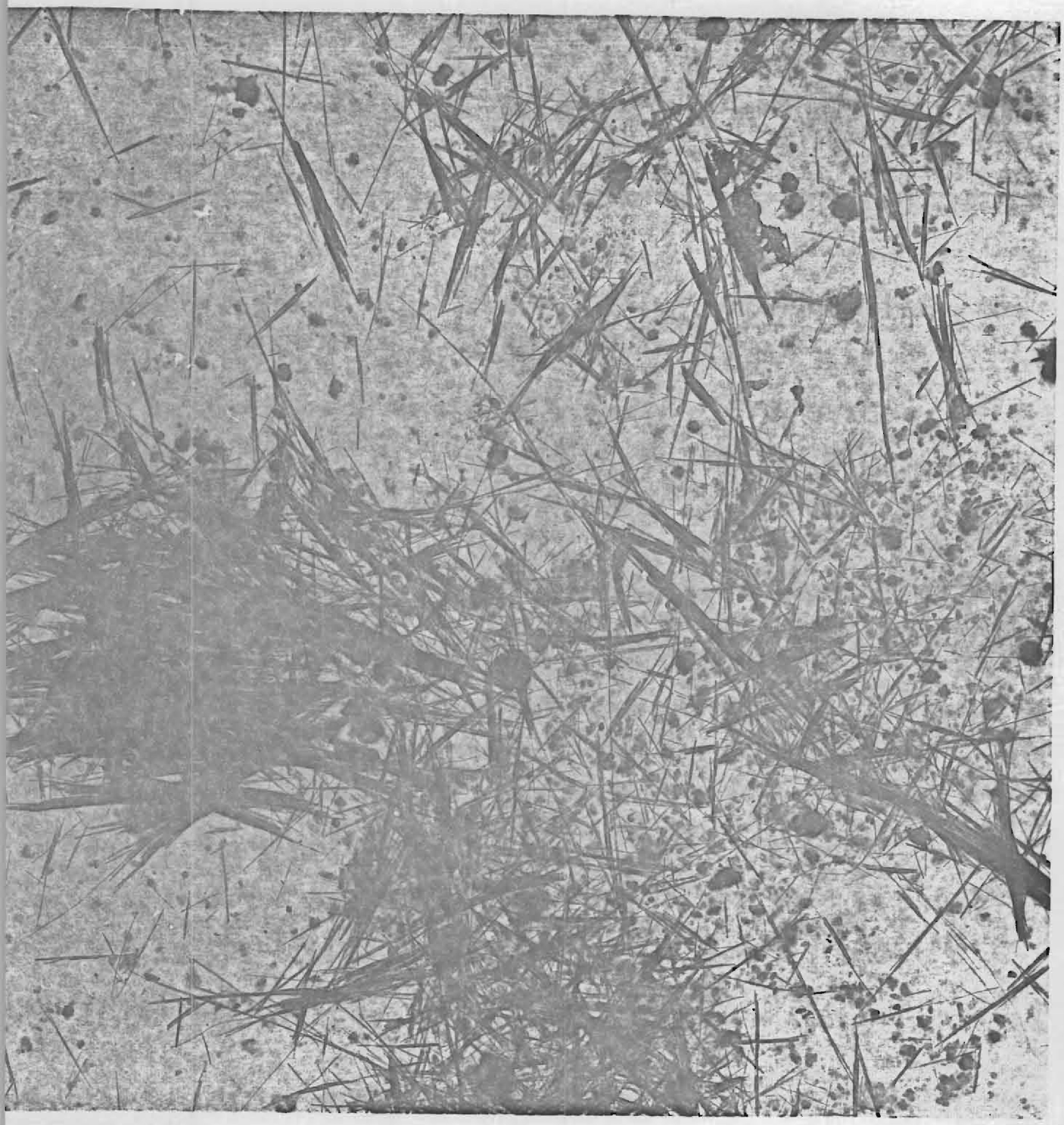

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Fig. 2 Electron Microphotograph of
-325 Mesh Portion of Matrix

FINAL REPORT
Project A-1208

RECOVERY OF ATTAPULGITE FROM PHOSPHORITE MATRICES

By M. F. Munoz
Senior Research Engineer

October 13, 1969 to April 30, 1970
Issued May 11, 1970

Preparod for
KERR-MCGEE CORPORATION

1970

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

FINAL REPORT

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RECOVERY OF ATTAPULGITE FROM PHOSPHORITE MATRICES

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OCTOBER 13, 1969 TO APRIL 30, 1970

ISSUED MAY 11, 1970

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KERR-MCGEE CORPORATION

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INTRODUCTION

The purpose of the work was to determine whether attapulgite clay present in phosphorite matrices, found in the property of the sponsor, could be separated economically from the non-clay constituents of the matrix.

In order to accomplish this, Project A-1208 was established with the following research program:

1) Characterization of the clay sample.

2) Feasibility determinations on the recovery of attapulgite.

3) Evaluation of selected recovered products.

The study, due to its preliminary feasibility goals, required flexibility in the investigation program. The experimental methods followed to recover the attapulgite included physical separations such as high intensity magnetic and physico-chemical such as flotation. Work reported in Project Report of January 31, 1970 indicated the feasibility of producing a pet-litter or floor sweeping compound from the minus 200 mesh fraction of the matrix.

This Final Report covers the work during the period from January 31, 1970 to April 20, 1970. Results of this study confirm experimental data obtained at the Georgia Institute of Technology for the South Georgia Minerals Program concerning the difficulties caused by attapulgite indurated particles ("chips") in the separation by froth flotation of phosphorite from the clay and quartz sand gangue 1/.

TECHNICAL CONSIDERATIONS

Structure

Attapulgite is the principal clay mineral from the group of clays known collectively as fuller's earth. Attapulgite - a hydrated magnesium aluminum silicate with the formula $3MgO \cdot 1.5Al_2O_3 \cdot 8SiO_2 \cdot 9H_2O$ - has a unique chain structure - different from the typical flat layer structure of other clays such as kaolinite. The chain structure imparts mineral properties in the colloidal size range unmatched by any other mineral. The sorptive characteristics of this clay are also unusual. Since the chain structure of attapulgite is three-dimensional, it cannot swell like montmorillonite, a layered silicate. The needle-like habit is due to the cleavage along the Si-O-Si bonds which holds the chains together. The attapulgite needles have lengths approximately 1 micron long and 0.01 micron wide. The colloidal properties are largely due to the channels that run parallel to the long axis of the needle-like particle. These channels contain water, loosely bound, and when this loosely held water (or zeolitic water, since it fills channels similar to the ones found in zeolites) is removed, cross sections of about 3.7 by 6.0 Å, have been estimated for the channels 2/.

Commercial Types of Attapulgite

Crude attapulgite, as mined in the Attapulgus (Georgia) and Quincy (Florida) areas is not as pure clay as are the kaolinites mined along the Fall Line. There are two main grades of attapulgites, colloidal grades and sorptive grades; Table IX shows data on these two main types.

Colloidal grades are dried at mild temperatures after crushing and gross removal of impurities. Drying for long periods of time at temperatures higher than 100°C causes the combined or zeolitic water to start leaving the channels and as a result the channels collapse. This causes loss of colloidal properties. In practice, rapid drying with hot air (400°C) in rotary dryers, is used to produce attapulgites for petroleum drilling mud 2/. Wet processing (extrusion) of the clay can be done before drying. This treatment is said to increase the viscosity, decolorizing and filter-aid properties of attapulgite.

Sorptive grades are produced at higher temperatures and can be further purified by grinding in Raymond Roll Mills.

Attapulgite's unique properties lie in:

1) High sorptivity of calcined grades.
2) Little effect of electrolytes on stability of aqueous dispersions.
3) Forming stable colloidal suspensions of high viscosity at low solids concentrations.
4) Chemical inertness.

Uses of Attapulgite

The uses of this clay mineral are numerous, and can be classified into three major classes 2/:

1. Colloidal Applications: In surface coatings, and as a thickening, antisag, and/or leveling agent; in adhesives, sealants and putties as thickener, and in non-sagging sealers; and as drilling muds when salt formations must be drilled (montmorillonoid clays do not maintain their viscosity in high monovalent ion concentrations, but attapulgites are practically unaffected by these salts).

In the stabilization of suspensions and emulsions, attapulgites have been successful in the suspension of slurry fertilizers in levels of 2-3% clay. In liquid fertilizers, attapulgite has been used to suspend iron and aluminum phosphates (impurities from the wet-process acid) which otherwise will settle down 3/. As thickening and gelling agents, attapulgite is used with organic and aqueous liquids. As a binder it is used in foundry sands and also cosmetics.

Attapulgites have also been used as fillers for elastomers and foams.

2. Sorptive Applications: Decolorization of liquids such as oils, fats, waxes, resins, vitamins, brewery products, water, and industrial and sewer wastes 2/. Attapulgite also has been used successfully in paper reclaiming, and conditioning and coating of fertilizer prills. Pesticide carrier and filter aids are among other applications. Cleaning products such as sweeping compounds, dry powder rug and upholstery cleaners, and many others have attapulgite as an ingredient.

3. Catalytic Applications: NCR paper, or "no carbon required" is a patented application of attapulgite, and its largest catalytic application. Other uses in this field include petroleum and chemical processing.

EXPERIMENTAL PROCEDURE

1. Preparation and Characterization of Matrix Sample

Approximately 1,000 pounds of matrix sample were received in water tight bags. The contents of each bag were chopped into 1/2 inch pieces and placed back into the original bags. When the contents of all the bags were processed, the total amount of matrix sample was mixed on a platform using the cone-and-ring method. After mixing, the matrix was placed back into sealed containers to prevent water loss by evaporation.

Representative samples of the matrix were taken for the characterization work. Table I shows the result of moisture, pH and dry density of the matrix sample. Results shown are the averages of two determinations. Figure No. 1, Characterization Flowsheet, shows details of the procedure followed. A sample of matrix was dispersed with a 0.5% solution of tetrasodium pyrophosphate (TSPP), and care was taken not to stir the clay excessively and thus decrease the size of clay particles, but rather allow the dispersant to act on the matrix minerals by itself. The supernatant liquid containing only clays were collected and mixed with the rest of the clays, obtained by washing and decanting from the bulk of the matrix. The supernatants were passed through a 325 mesh sieve to make sure no coarse particles were carried over. The rest of the sample (the +325 mesh portion) was dried in an oven at 90°C, and screened through the following Tyler Mesh sieves: 4, 8, 16, 28, 35, 48, 65, 100, 150, 200, 270, and 325. After recording the weights, the -325 portion collected in the pan was added to the rest of the -325, flocculated, dried and weighed. Table II shows the screen analysis data. Each one of the screen cuts coarser than 325 mesh was placed in a suitable bottle with enough 0.5%

tetrasodium pyrophosphate to make approximately a 50% (by volume) slurry. Each bottle was placed in a mechanical shaker and agitated for 20 minutes to disperse the clay chips with a minimum amount of grinding for the other minerals present. When no clay particles were detected, the sample was carefully washed through a 325 mesh sieve. After taking a small sample of clay for x-ray diffraction analysis, the +325 mesh fractions were dried at approximately 90°C. After weighing the non-clay (+325 mesh) fractions of each screen cut, the clay (-325 mesh) fractions were determined by difference. The weight percent of clays and non-clays is presented in Table II. Weight distribution of clay and non-clay material as well as the weight percent of clay in each particle size fraction on the basis of the weight of the fraction are shown in Table III and Figure 2.

2. Recovery of Attapulgite

Flotation techniques were used in order to separate the attapulgite "chips" in the 16 x 200 mesh cut of the matrix into a flotation concentrate before the flotation of phosphorite. Table V shows the parameters of a typical flotation test. Dry magnetic separation tests were made on the 16 x 48, 48 x 100, and 100 x 200 mesh cuts of the dry feed, using a Carpco high intensity dry magnetic separator. This apparatus reaches magnetic field intensities up to 11,000 gauss. Results are presented in Table VI. Attrition scrubbing tests were also made on the total matrix, by varying the Denver Laboratory scrubber RPM, and keeping solids slurry concentration and scrubbing time constant. Table VII shows results of these tests.

3. Evaluation of Recovered Products

Two types of products were considered: a rough -200 mesh concentrate, which was flocculated, dried, ground and fired to produce a low-cost pet-litter or floor sweeping compound, and a -325 mesh product which was dried without the addition of any flocculant. The tests performed on the -200 mesh concentrate were reported in the partial report of February 6, 1970. Table VIII presents data on the optimum amount of flocculant necessary for dewatering prior to drying.

Typical physical properties of commercial attapulgus clays were determined on the -325 mesh concentrate. These included free moisture loss at 220°F (104°C), volatile matter loss at 1200°F (649°C), ignition loss at 1832°F (1000°C), specific gravity, tamped bulk density and surface area (BET). Analysis of surface area on samples of -325 mesh were started after drying at 90°C to avoid any loss of combined water. It was determined after more than a week of testing that the vacuum on the chamber was insufficient for valid results even with heating the sample to 250°C. The large amount of organic matter present was believed responsible for the failure of the test procedure, hence another sample was treated with H_2O_2 at 90°C to remove the organic matter. Surface area determinations, obtained at 300°C, are shown in Table IX, along with some published values for commercial attapulgites.

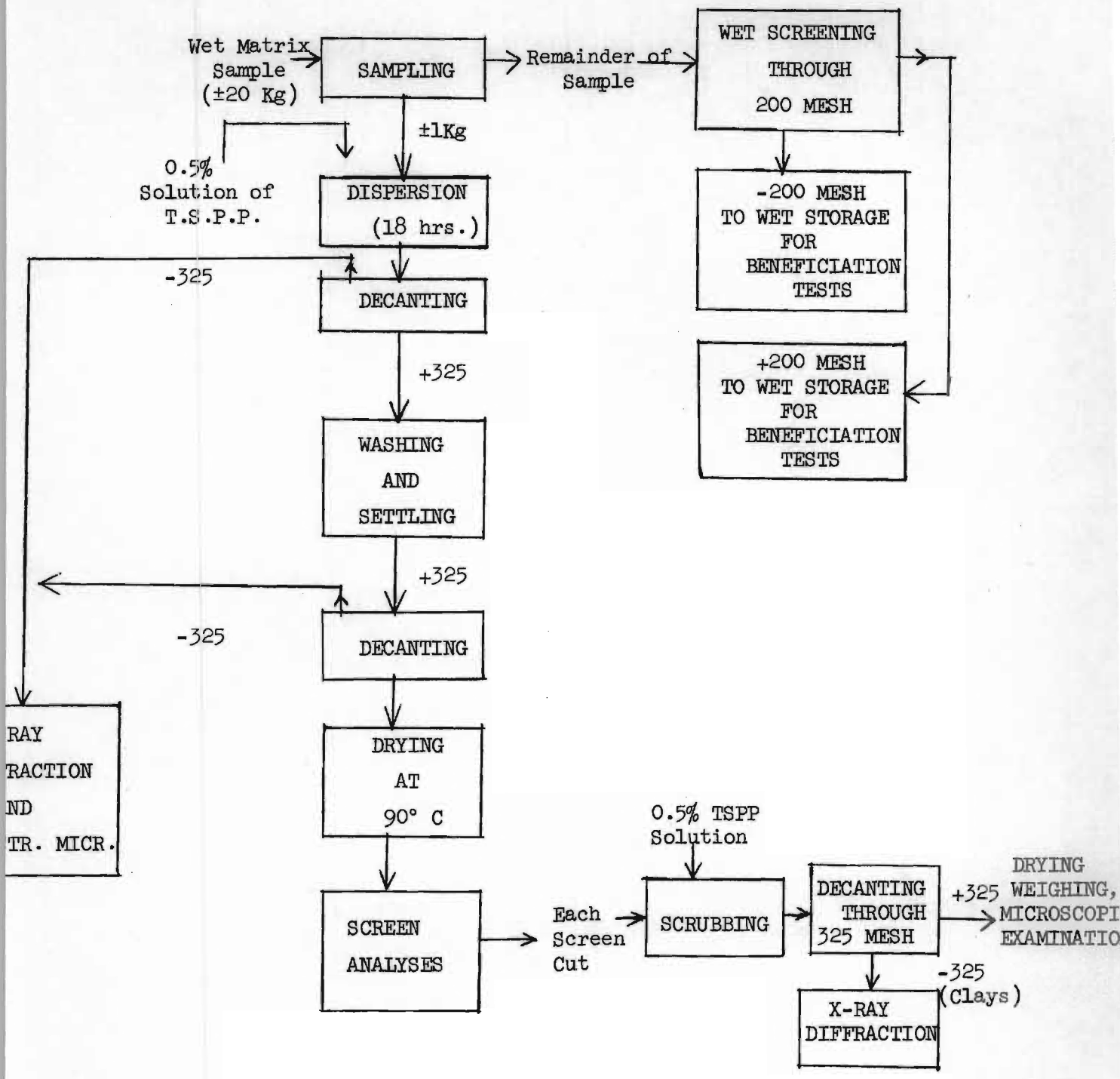

Figure No. 1 Characterization Flowsheet

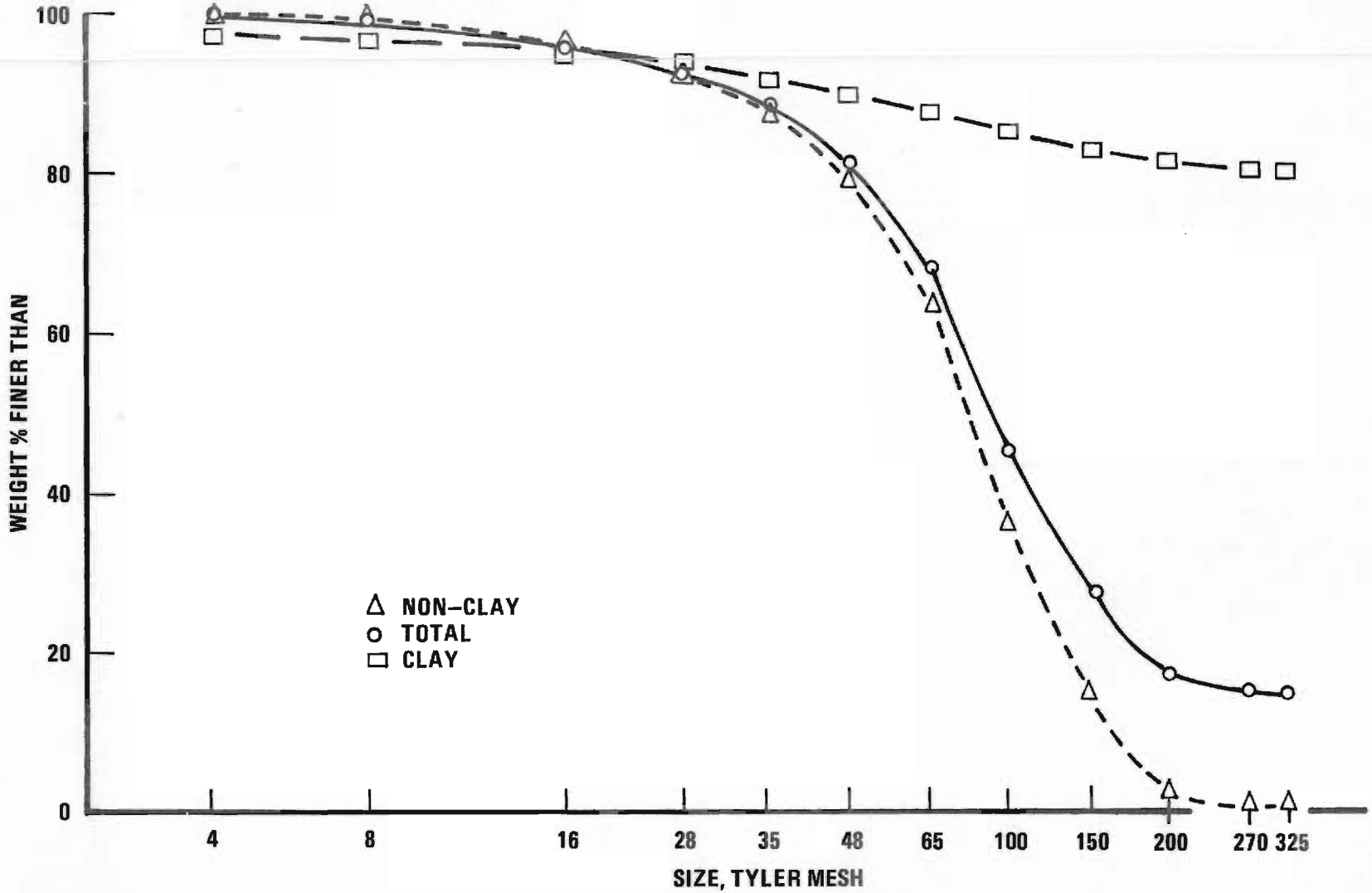

Figure 2. Particle Size Distribution of Matrix Components

TABLE I

MOISTURE, PH AND DRY DENSITY OF

MATRIX SAMPLE AS RECIEVED

Moisture:	27.2%
pH:	7.8
Dry Density:	78.4 lb/cu. ft.

TABLE II

SCREEN ANALYSIS OF

MATRIX SAMPLE

Retained on Tyler Mesh	Weight %	Weight % Clay	Weight % Non-Clay	Cumulative % Weight
4	0.6	0.4	0.2	0.6
8	0.7	0.2	0.5	1.3
16	2.8	0.3	2.5	4.1
28	3.5	0.3	3.2	7.6
35	4.1	0.3	3.8	11.7
48	7.2	0.4	6.8	18.9
65	12.9	0.4	12.5	31.8
100	22.9	0.5	22.4	54.7
150	17.6	0.4	17.2	72.3
200	10.3	0.3	10.0	82.6
270	2.1	0.1	2.0	84.7
325	0.4	0.0	0.4	85.1
Pan	14.9	14.9	0.0	100.0
Total	100.0	18.5	81.5	

TABLE III

CLAY CONTENT AND DISTRIBUTION

ON SIEVE FRACTIONS

Retained on Tyler Mesh No.	Weight % Clay of Fraction on Sieve	% Distribution of Clay	% Distribution of Non-Clay
4	70.0	2.1	0.2
8	34.1	1.4	0.6
16	9.0	1.4	3.1
28	8.3	1.6	4.0
35	7.5	1.7	4.6
48	5.0	1.9	8.4
65	3.3	2.3	15.3
100	2.1	2.6	27.6
150	2.2	2.1	21.1
200	3.0	1.7	12.2
270	6.2	0.7	2.4
325	9.3	0.2	0.5
Pan	100.0	80.3	0.0
Total		100.0	100.0

TABLE IV

MINERALOGICAL ANALYSIS OF CLAY IN +325 MESH FRACTIONS

MINERALS IDENTIFIED (*)

Fraction Retained On Tyler Mesh No.	Atta-pulgite	Sepio lite	Illite	Kaol-inite	Montmor-illonite	Quartz	Dolomite	Apatite
4	M	T			m	m	m	T
8	M	T			m	T	m	T
16	M	T		T	M	T	m	
28	M	T		T	M	T	m	
35	M	T			M	T	m	
48	M	T			M	m	m	T
65	M	T	T		M	m	m	T
100	M	T	T		M	T	m	T
150	M	T	T	T	M	T	T	T
200	M	T	T	T	M	T	T	T
270	M	T	T	T	m	T	T	T
325	M	T		T	M	T	T	
-325	M	T			M	T	m	

* M = Major component; m = Minor component; T = Trace

TABLE V

PARAMETERS OF CATIONIC

FLOTATION OF ATTAPULGITE CHIPS

Test No. CF-7

Sample = 35 x 200 mesh matrix

Charge Dry Weight = 250 g

Conditioning slurry pH = 7.5

Solids concentration = 20% Machine = Denver D-1 Flotation Machine

Conditioning Time = 15 seconds Speed = 900 RPM

Reagents	lb/ton
Armeen "C" acetate	0.2
Kerosene	0.1
Pine Oil	0.1

Flotation

Machine = Denver D-1 Speed = 1000 RPM

Time = 2 minutes

Observations = Very loose froth, yellow-greenish, containing very fine clays. Very little clay "chips", and some sand and phosphorite grains floated.

TABLE VI

DRY MAGNETIC CONCENTRATION

OF ATTAPULGITE

Tyler Mesh Screen Cut	% Weight of Clay on basis of Screen Cut Weight	% Weight Magnetic Concentrate	Approx. Clay % Distribution in Magnetic Conc.	% Weight Non-Magnetic Concentrate	Visual Comments
16 x 48	20.8	7.1	20	92.9	Magnetic concentrate is approximately 2/3 clay. Non-mags. contain much clay.
48 x 100	5.4	6.7	40	93.3	Magnetic concentrate is approximately 1/3 clay. Non-mags. fairly clean.
100 x 200	5.2	7.9	75	92.1	Magnetic concentrate is approximately 1/2 clay. Non-mags. look clean.

TABLE VII

SCRUBBING DATA

Test No.	Speed, RPM	% Solids	Time, Min.	Weight of +200 Mesh Scrubbed Material (gms.)	Observations
Sc-1	900	30	15	205.3	Quite a lot of clay chips in +200 fraction, plus mud balls.
Sc-2	1200	30	15	209.6	Less clay chips than Sc-1 and chips were smaller in size.
Sc-3	1500	30	15	206.9	Less clay chips than Sc-2, plus one mud ball.
Sc-4	1800	30	15	204.2	Less clay chips smaller in size than the ones in Sc-3, plus one mud ball.
Sc-5	2100	30	15	203.9	Clean of clay chips except for one mud ball.

TABLE VIII

FLOCCULATION DATA

Sample: -200 mesh slimes

Amount: 300 ml. slurry containing 9.9 gm. dry solids

Flocculant: American Cyanamid Company's Superfloc 16

Mode of addition: Flocculant solution (0.0116 gm. dry Superfloc 16 per ml. solution) added dripwise.

pH of slurry: 7.7

pH modifier: HCL and NaOH when indicated.

Test No.	pH	Weight % Dry Solids in Slurry	Optimum Weight of Flocculant Necessary, gm.	Optimum Amount of Flocculant in Lbs. Dry Flocculant Per Short Tons of Dry Solids
Sp-1	7.7	3.24	0.348	70.3
Sp-2	5.7	3.24	0.348	70.3
Sp-3	6.7	3.24	0.348	70.3
Sp-4	8.7	3.24	0.348	70.3
Sp-5	9.7	3.24	0.348	70.3
Sp-6	7.7	1.62	0.058	11.7
Sp-7	7.8	1.09	0.0406	8.2
Sp-8	7.7	1.62*	0.0116	2.3

* The stock 3.24% slurry was diluted with 300 ml. of clean supernatant from Test Sp-6.

TABLE IX

PHYSICAL PROPERTIES OF -325 MESH

CLAY CONCENTRATE AND SOME COMMERCIAL

ATTAPULGUS CLAYS

	K-M Sample	Commercial Grades Per Literature			
			Sorptive Grades		
Physical Property	-325 Mesh Clay Concentrate	Colloidal Grade High Volatile Matter	Regular Volatile Matter	Low Volatile Matter	Very Low Volatil Matter
Free Moisture, % loss at 220°F	10.0	10-17	3- 7	0	0
Volatile Matter, % loss at 1200°F	10.4	10	7	2-5	1-3
Ignition loss % at 1832°F	1.7	22- 5	12-16	6-10	4-6
Specific Gravity	2.35	2.3-2.4	2.3-2.5	2.3-2.5	2.3-2.5
Bulk Density, Tamped, lb/ft^3	22.1	19-45	28-36	28-36	28-36
Surface Area, BET, $m.^2/g.$	104.2 (*)	210	125-135	125-135	125-135

* This sample was treated with H_2O_2 to eliminate the organic matter at 90°C. The surface area determination was carried out at 300°C because degassing at 90°C was not feasible.

DISCUSSION OF RESULTS

1. Characterization of Matrix Sample

Dry Density and pH. The values obtained in determinations of dry density for the matrix sample are within the published values obtained from Chatham County phosphorite matrices 4/. pH values measured on the matrix sample are in the range of attapulgite clay pH 5/: this may be explained on the basis that probably the major ionic contributor to the liquid phase is the clay, since the other minerals present are not very soluble, but the clay may release substantial amounts of base-exchanged ions into the solution.

Particle Size. From Tables II and III, as well as from Figure 2, it can be seen that clay "chips" follow a size distribution that parallels the non-clays from about 8 mesh to about 325 mesh. The "free" clays - that is, the clays not forming disintegration-resistant chips, are very abundant below 325 mesh in such a way that the total clay may have a bimodal distribution, with one mode at about 100 mesh and another below 325 mesh. Clay "chips" are fairly constant in weight through the range 4 to 200 mesh, although the percent of weight is never higher than 0.5. Some of the "chips" are soft enough to slime continuously and contribute to the clays present in the -325 mesh fraction. It should be noted from Table III that the coarse fractions (+4, 4 x 8 mesh) contain much more clay on the basis of sieve fraction weight than the other size ranges (except for the -325 mesh fraction).

Mineralogical Analysis. The results presented in Table IV indicate that attapulgite is the major mineral constituent of the clays throughout the size range. Montmorillonite, and to a minor extent dolomite, accompany the attapulgite in amounts varying from trace to major constituent in all

the particle sizes. Smaller in amount, but also present through the particle size range, are quartz and sepiolite. The minerals identified in the clays are the same accessory minerals found in the attapulgus clay as mined, except for the traces of apatite found. The presence of these traces may be explained as a slight contamination of apatite from the phosphorites on the scrubbing operation. Mineral content for attapulgus clays, as mined, are reported to be "70 to 80% attapulgite; 10 to 15% montmorillonite, sepiolite and other clays; 4 to 8% quartz; and 1 to 5% calcite or dolomite 2/".

2. Recovery of Attapulgite

Flotation. The flotation of the clay "chips" was first attempted using cationic reagents such as amines. Two reagents were tried: Armeen "C", (100% neutralized with acetic acid) and unneutralized Amine 750. The first amine is a commercial dodecylamine made from coconut oil, manufactured by Armour and Company, and the second one is an abietyl amine, made from pine rosins by Hercules Powder Company. Both products are widely used in industry. Typical results, as shown in Table V, indicate that even with short conditioning time and high dilution of the slurry to avoid sliming, the result was a very poorly loaded froth, very scarce in clay "chips" since some of the "chips", the softer ones, slimed readily, and therefore used up all the amine available, leaving behind the hard clay particles. Some of the quartz and phosphorite also floated. A few tests were made with fatty acids since the clay chips may have positive charge zones on the surface due to the presence of magnesium and calcium ions in the clay. The fatty acid (Indusoil M-28) was added in starving amounts, in the form of a soap, but the attrition resulting from the mixing action in the cell again produced slimes with no concentration of consequence.

Due to the low concentration of clay in the flotation feed (See Table III) and the tendency of some of the "chips" to slime, the attempts to concentrate attapulgite by flotation were considered infeasible and were not continued.

Magnetic Separation. The dry magnetic separation determinations that were performed on the 16 x 48, 48 x 100 and 100 x 200 mesh cuts of the matrix had interesting results. It is known that dry magnetic separation of phosphorite concentrates will yield a small magnetic concentrate differing only in the increased amount of iron oxide and alumina from the bulk of the concentrate 1/. Therefore it was expected that the magnetic fraction produced in the above screen cuts of core matrix would contain only the phosphorite higher in iron than the rest, plus any heavy mineral present high in iron such as ilmenite, magnetite etc. Instead, as Table VI shows, a concentration effect takes place in the clay screen cuts also. The concentration effect increases as particle size decreases. Although the industrial use of this dry magnetic separation technique may not be economically feasible, research on wet high intensity separation (Carpco, Jones or Eriez separators) may prove rewarding.

Scrubbing. Scrubbing tests were conducted at 30% solids, since preliminary tests indicated that 30% was the highest concentration of solids at which the attrition scrubbing could be done effectively in the Denver Laboratory Scrubber. Results of scrubbing tests performed on total matrix, at 30% solids indicate the following:

1) Increased RPM of the scrubber with constant solids content and scrubbing time seems to correlate with elimination of clay chips.

2) Clay balls were not affected by the scrubbing action due to the geometry of the scrubber. These balls lodged on the wall of the tank between the impeller blades, and the flow of the sand and phosphorite slurry did not seem to affect their degree of dispersion. Previous experience with matrices from Chatham County, Georgia pointed to the fact that a log washer is sometimes more effective in removing these clay balls than the scrubber. These remarks apply, of course, to laboratory-sized equipment, and may not be true of plant or pilot plant sized equipment.

3) Two washings were enough to remove most of the dispersed clays from the phosphorite and sands.

Flocculation. The flocculation data shown in Table VIII point out the inter-relationship between concentration of solids and optimum amount of flocculant necessary for separation of the two phases.

The lowest concentration of flocculant found to produce the necessary separation was 2.3 lb/ton of dry clay. This was attained by using supernatant liquid from another test to dilute the solids concentration. It is believed that use of larger tanks with slow revolving paddles, not available at the time of this investigation, will show lowered concentration of flocculant to do the job.

The following comments apply:

1) Slow, continuous agitation promotes the formation of flocs and therefore decreases the amount of flocculant.

2) The flocculant dosage is decreased when added to a portion of the clay and then, the flocculated clay added in turn to the bulk of the slurry.

3) Data shown in Table VIII suggest that a "certain" quantity of flocculant has to be added to obtain good flocculation, even if presence of the

flocculant in the supernatant indicates that less than the "certain" quantity was used in actually flocculating the mineral.

4) Table VII also indicates that substantial savings in the use of flocculant can be obtained if the supernatant liquid is re-used, and as pointed out above in No. 2, mixed with the clay before addition. By re-using the supernatant (or filtrate as the case may be) it may be possible to keep flocculating the clay by suitable additions of reagent to the filtrate.

5) Extrusion of the filter cake as "spaghetti" prior to drying may decrease the amount of grinding.

6) The flocculant chosen for these tests have been extensively tested in flocculation of clays at Georgia Tech, and found effective at lower concentrations than other reagents. The flocculant, Superfloc 16, manufactured by American Cyanamid Company, is a polyacrylamide, effective in both low and high values of pH.

7) The nature of the flocs formed by the attapulgites somewhat follow the needle habit of the clay particles, and form, when excess of flocculant is added, stringy, ropelike flocs which are very easy to separate from the liquid phase.

Physical Properties of Uncalcined Clays. Table IX presents some physical properties used in determining the suitability of attapulgite clays for certain uses. As it can be seen from that table, the -325 mesh portion of the matrix on the basis of the tabulated properties shows a strong possibility for a colloidal grade attapulgite. It should be remembered, however, that this portion contains a substantial amount of montmorillonite, and that the removal of montmorillonite in that particle size range can be extremely

difficult. The value obtained in the surface area determination of the -325 clay concentrate is low relative to the value presented for the colloidal attapulgite. The published surface area data shown in Table IX had no information about the temperature at which the surface area was determined.

The surface area value shown for the -325 mesh clay concentrate was obtained at 300°C, since attempts to degas the sample, even after eliminating the organic material with hydrogen peroxide, at lower temperatures starting at 90°C, took several days.

The interpretation that can be given to this low surface value, obtained at a relatively high temperature (300°C), is that the clay in the colloidal condition has much more surface area available than the value measured, since the channels of the colloidal, crystalline attapulgite collapse gradually as the temperature increases over 200°C. Thermal treatment of attapulgite at about 100°C has been reported to produce decreases in surface area from 192 m^2/g. before treatment to 128 m^2/g. afterwards.

Therefore, the surface area of the clay concentrate, if amenable to be measured at temperatures below 90°C, may well be over 150 m^2/gm. Success in the use of this -325 mesh clay concentrate for a given application may be the only criterion that can be applied. Therefore, the results of this study indicates the possibility of making two types of products out of the attapulgite from the Chatham matrices:

1) Flocculation of the -200 mesh portion of the matrix to produce a cake after filtration which extruded as "spaghetti", dried, fired at 900°F, ground and screened can be sold for pet litter or floor sweeping compound.

The fines produced could be used in coating of fertilizer prills or pesticide carriers.

2) Processing of the -325 mesh portion of the matrix may produce a colloidal attapulgite. Applications where fairly dilute attapulgite slurries are needed should be preferrably considered because of the cost involved in drying this material without the benefit of flocculants. Flocculants may impair some of the desired properties of the attapulgite, such as high viscosity. Although it is reported in the literature that heating at "high" temperatures makes attapulgite lose its colloidal characteristics 3/, rapid drying with hot air about 400°C and simultaneous disintegration into coarse particles has been reported for attapulgite used in petroleum drilling mud 2/, which needs the colloidal character of the clay.

CONCLUSIONS

1. The clay "chips" have a particle size distribution similar [in shape] to the particle size distribution of the non-clays in the matrix. The "chips" and the -325 mesh portion of the clays form a bimodal distribution curve.

2. The clay "chips" present in the plus 200 mesh portion of the matrix are only 3.6% of the total matrix and 19.7% of the total clay portion of the matrix. The chips have only nuisance value as they have to be removed to produce a clean phosphorite flotation feed.

3. Flotation of clay "chips" was not feasible.

4. Dry magnetic separation of clay "chips" produced concentration of the "chips" in the magnetic concentrate. Degree of concentration increased as size decreased in the size range tested.

5. Attrition scrubbing methods proved successful in cleaning the phosphorite flotation feed from clay "chips". Of the three variables: (1) solids concentration, (2) scrubbing time, and (3) speed of scrubbing (RPM), maximum efficiency was attained by holding the first two constant and increasing the third.

6. A pet litter or floor sweeping compound may be produced from the -200 mesh portion of the matrix.

7. More work is needed to determine whether the -325 mesh portion can be a source of colloidal grade attapulgus clay.

RECOMMENDATIONS

1. High-intensity wet magnetic separation of attapulgite should be investigated.

2. Scrubbing should be tested at the pilot plant level to find the effect of scrubbing vessel size on the efficiency of the operation.

3. It is recommended that pilot plant size studies be carried out for the manufacturing of the pet litter or floor sweeping compound product, and that the extrusion of the -200 mesh filter cake as rods, prior to drying, be evaluated as an auxiliary method to crushing.

4. It is recommended that the -325 mesh clay concentrate be evaluated for specific applications (such as drilling muds) as a colloidal attapulgite.

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